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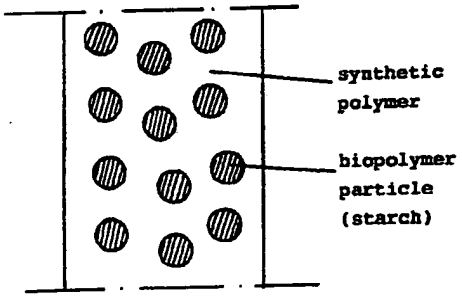

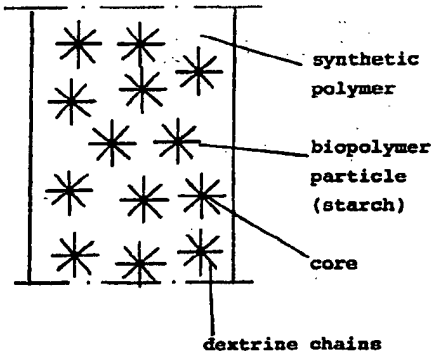

(57) Abstract

The inventi n relates to a bi logically decomposable composition, comprising a composition consisting of a biopolymer and a synthetic polymer, the composition further including a material causing in certain conditions disintegration f the chains of the synthetic polymer and/or the synthetic polymer of the composition being treated in a manner that the chains of the synthetic polymer disintegrate in certain conditions. The biopolymer is enzymatically modified.

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Biologically decomposable composition

The present invention relates to a biologically decomposable composition, comprising a composition consisting of a biopolymer and at least one synthetic polymer, the composition further including a material causing in certain conditions disintegration of the chains of the synthetic polymer and/or the synthetic polymer of the composition having been treated in a manner that the chains of the synthetic polymer disintegrate in certain conditions.

This type of biologically decomposable composition is disclosed e.g. in GB Patent Specifications 1 487 050, 1 485 833 and in US Patent Specification 4 337 181. In this case, to a biologically decomposable composition is added some self-oxidizing agent containing at least one double-bond which, when contacted with a metal salt, produces reactions as a consequence of which the composition decomposes when placed in the ground. In the cited publication, the biopolymer used is starch. However, the use of starch as set forth in the cited publication is highly unfavourable especially when the purpose is to provide films having a good tensile strength but at the same time biologically decomposable characteristics.

Publication EP-230143 discloses a synthetic polymer decomposing agent which is sensitive to light. The additive disintegrates polyethene chains as the composition is exposed to light. Thus, polyethylene will be decomposed as it is exposed to the effect of light for a lengthy period of time.

The above deals particularly with mechanisms for chopping the synthetic polymer in a biologically decompos-

able composition. Thus, this can be effected either by means of an additive incorporated in a composition for cutting off in certain conditions the chains of a synthetic polymer or by treating the synthetic polymer itself in a manner that the polymer chains break in certain conditions. It is natural that a combination of the above factors can be utilized. The most important reason for these treatments is that certain synthetic polymers, such as polyethylene polymer, do not decompose microbiologically. For example, in a composition disclosed in GB Patent Specification 1 485 833, the synthetic polymer surrounds starch particles (biopolymer). A consequence of this is that the organisms decomposing starch particles are not able to make at least a direct contact with starch, since said organisms do not penetrate the layer of synthetic polymer. Thus, the disintegration of the polymer chains of such layer of synthetic polymer is extremely essential, so that the organisms capable of cooperation with biopolymer can make contact with biopolymer. Hence, especially starch particles turn gradually into glucose as a result of microbial actions. The resulted glucose is used by microbes as a source of carbon and energy. The hydrocarbon chains chopped from a synthetic polymer, such as polyethylene, can serve as a source of carbon and energy for the microbes.

Thus, for the above reasons, it is essential to incorporate in a biologically decomposable composition and/or its synthetic polymer a "triggering" factor which decomposes the synthetic polymer.

A problem with biologically decomposable compositions of the prior art is, however, that the biopolymer contained therein consists of starch particles which have

a relatively large size and a relatively small reactive surface. When manufacturing plastic films, for example, the large biopolymer particles considerably impair the strength characteristics of a film. In addition, decomposition of such compounds is very slow because of small active surface area.

An object of this invention is to provide a biologically decomposable composition which to the maximum extent overcomes the weaknesses of prior known compositions. In order to accomplish this object, a biologically decomposable composition of the invention is mainly characterized in that the biopolymer is ezymatically modified.

The advantage gained by the invention can be clearly seen e.g. when the biopolymer used is starch. Starch can be enzymatically modified so that the surface of starch particles is only partially hydrolyzed. In partial hydrolysis, on the surface of a particle around he diminishing core develops a dextrine chain layer which has the effect that, in theory, the particle "dissolves" without any boundary surface in a synthetic polymer, such as polyethylene. When such a composition is exposed to conditions favourable to decomposition, the polymer chains of a synthetic polymer disintegrate e.g. as a result of the action of UV-light, whereby the particlly dissolved starch together with pieces of the chains of a synthetic polymer provides a culture medium favourable to microbes. The glucose, which first develops from dextrines in biological suggession, brings over a relatively fast-growing microbism. That collects near the synthetic polymer also other growth factors which, when starch is used up, are also required by those microorganisms which use as their

source of carbon th carb n chains formed from a chopped synthetic polymer. As an example there is shown the following diagram, wherein the biopolymer is enzymatically modified starch and the synthetic polymer is a polyethylene film comprising a structure decomposing it in UV-light

UV-starch-polyethylene film

↓ UV-radiation

polyethylene pieces + dextrine-coated starch particles

↓ Amylolytic microbes

polyethylene pieces + nutrients

↓ "Ethenolytic microbes"

end product e.g. CO_2 + H_2O + biomass

One of the most significant advantages gained by the invention is that by means of enzymatic modification the particle size of a biopolymer can be adjusted as desired. In principle, this means that the actual core of a particle diminishes especially when starch is used and around the core there is grown a dextrine chain layer. Thus, the amount of biopolymer in relation to synthetic polymer can be increased without impairing the mechanical properties of a composition. This is due to the fact that the enzymatically modified biopolymer sort of dissolves in synthetic polymer. The biopolymer treating enzyme remains as stable on the surface of biopolymer particles in partial hydrolysis. The enzyme is activated by the action of water, whereby the starch dissolves and it is a microbiologically readily available source of energy. The enzymatic-

ally modified biopolymer can be dried so it can be readily mixed within synthetic polymer granulate and extruded into a plastic film.

As pointed out above, one preferred biopolymer is starch. An enzymatic modification on starch according to the invention can be preferably effected with alfa-amylase, e.g. α-1,4 glucan-4 clucan-hydrolase: (E.C. 3.2.1.1.) particularly with heat-resistant alfa-amylase. A characteristic feature of heat-resistant alfa-mylase is that its action activates as temperature is rising and the thermal denaturation of an enzyme protein is very slow as it is bound to substrate (starch). The alfa-amylase enzyme remains bound to its substrate as high as at 180°C, i.e. for example at polyethylene film production temperature, for a sufficiently long period of time so as not to be destroyed in the production of film.

Another preferred biopolymer is cellulose. The enzyme used for its enzymatic modification is cellulase, e.g. 1,4- β-D-glucan cellobiohydrolase: (E.C. 3.2.1.91.), especially a cellulase that form cellodextrines.

The invention is further illustrated in the accompanying drawing showing diagrammatically the effect of the enzymatic modification of biopolymer particle on the structure of such particle. The top of fig. 1 (2) shows biopolymer particles prior to modification and as they would be incorporated e.g. in a film-making process in the prior art solutions. Furthermore, the bottom (b) of fig. 1 shows biopolymer particles obtained by enzymatic modification. Both groups of particles are provided with vertical lines on ither side thereof for describing the boundary surfaces of e.g. a produced

plastic film. As shown in the top figure, the biopolymer particle forms in the resulting film a cavity which significantly decreases the overall strength of a film at this point. On the other hand, a modified biopolymer particle, whose core is relatively small and which consists of members, such as dextrine chains (in the case of starch), branching off the core, does not produce a similar cavity effect on a plastic film and, thus, the strength impairing effect of a biopolymer composition is substantially lesser. Thus, it is possible to produce considerably stronger films with the same amount of biopolymer or to increase the amount of biopolymer without, however, impairing the strength characteristics of a film. In addition, fig. 1 shows one advantage of the invention, namely the fact, especially when starch is used, the dextrine chains extend at least in certain places all the way to the surface of a film providing for water a kind of capillary duct system directly inside the composition.

The following examples illustrate the manufacturing technique of a composition of the invention and results of the tests performed with the composition.

Enzymatic modification of biopolymer

EXAMPLE 1 Partial hydrolysis of starch

At the initial stage of modification 600 g (dry matter) of rice starch was suspended in a cold $CaCl_2$-solution containing 800 mg calcium/1 liter water. pH of the suspension was adjusted to 6,5. Temperature of the suspension was raised to 60°C with continuous agitation. A high temperature alfa-amylase enzyme produced e.g. by Bacillus licheniformis was added such an amount

in 25 ml that the mean particle size of rice starch decreased within 30 minutes from 30 um to below 10 µm. Suspension was cooled and cold-dried. The cold-dried enzyme-modified mass was ground e.g. in a mortar. The particle size distribution was determined e.g. with Malvern 2600 device for finding out a sufficient enzyme content.

EXAMPLE 2 Partial hydrolysis of cellulose

For modification, 300 g (dry matter) ofcrystalline cellulose was suspended in cold water. pH of the suspension was adjusted to 4,5. Temperature of the suspension was raised to 50°C with continuous stirring. [illegible] A cellubiohydrolase produced by Trichoderma reesei was added such an amount in 25 ml that the mean particle size of cellulose decreased within 30 minutes from 40 um to below 20 µm Suspension was cooled and cold-dried. The particle size distribution was determined e.g. with Malvern 2600 device for finding out a sufficient enzyme content.

The effect of enzymatic modification on the particle size is illustrated in the accompanying figure 2.

Preparation of biopolymer master batch and film-blowing

Enzymatically modified rice starch and polyethylene (film-blowing grade: melt index 1.8 and density 0.922) were mixed with each other at a ratio of 1:1. This mixture was melt stirred by means of a co-kneeter type of extruder from Buss AG (model MDK/E46 11D; screw length 506 mm; diameter 46 mm; screw temperature from forward end 140°C, 140°C, 140°C, 140°C). The melt mix-

ture of melt polyethylene and modified starch was finally compressed through the orifices (7 orifices, diameter 3 mm) at the end of the extruder and sliced by means of a cutter into a water basin by means of a cutter operating immediately downstream of the orifices and dried to form a master batch granulate.

In a similar fashion, the other biopolymers (rice starch, cellulose and modified cellulose) were used to prepare master batches containing 50 % of biopolymer.

Film-blowing was effected by means of a Luigi Bandera Uniblock type of 1-screw film-blowing extruder (screw length 1125 mm; diameter 45 mm; compression ratios 2,57:1 and 2.24:1; nozzle diameter 150 mm; nozzle slit 1 mm). The film-blowing conditions were as follows: temperatures from forward end of screw (set values) 130°C, 140°C, 140°C, 140°C, 140°C and 140°C; temperature of melt appr. 160°C; speed of rotation of screw 79 rpm; running speed 8-10 min and blowing ratio 1.8.

The above-described film-blowing extruder was used with varying biopolymer additions (1.5 - 6.0 % as dry) to preparepolyethylene films by employing a polyethylene grade whose melt index was 1.2 and density 0.922. The thicknesses of such manufactured films varied within the range of 70-90 μm (tables 1 and 2).

Table 1 indicates how the enzymatic modification of a biopolymer improves the mechanical strength properties of a film compared with polyethylene having enzymatically unmodified biopolymer added therein.

With rice starch, a 3 % addition provides a 30 % improvement in tensile strength, 20 % in elongation and

appr. 22 % in drop value. In addition, a film of modified rice starch (EMRT) is 5 µm thinner than a film of rice starch (RT). The change of particle size due to modification is also clearly seen in table 1 as the mean particle size of starch diminishes to about one fifth of the original.

Also with another biopolymer, i.e. with cellulose, the enzymatic modification provides similar improvements. The improvement in tensile strength by virtue of modification is appr. 24 %, in elongation nearly 20 % and in drop value more than 20 %. Also with cellulose, the particle size diminishes by virtue of modification to about half from the original.

TABLE 1

The effect of enzymatic modification of biopolymer (starch, cellulose) on the mechanical properties of a polyethylene film (pe-film)

Biopolymer	The amount of biopolymer in pe-film dry matter %	Tensile strength KS/PS (MPa)	Elongation KS/PS (%)	Drop value (g)	Mean part. size of biopolymer (µm)	Film thickness (µ)
RT	3.0	15.1/13.5	310/530	115	28.5	80
EMRT	3.0	18.8/17.9	370/640	140	6.0	75
S	4.5	12.7/10.7	280/500	95	36.9	90
EMS	4.5	15.9/13.1	340/570	115	18.2	90

RT = rice starch
EMRT = enzymatically modified rice starch
S = cellulose
EMS = enzymatically modified cellulose

Tensile str ngth and elongation measured with Instron device (model 1026) and results are given in accordance with the following standards:

Tensile str ngth KS = direction of film ASTM D882
PS = transverse direction "

Elongation "

Drop value ASTM D1709

Th mean particle size of biopolymer is determined with Malvern 2600 device in aqueous phase.

Table 2 indicates the effect of an increase in the amount of biopolymer on the mechanical strength properties of a polyethylene film.

With all different concentrations (1.5 - 6.0 %) the modified rice starch (EMRT) provides for mechanically stronger film properties compared to original rice starch (RT).

The difference between EMRT and RT increases dramatically as the amount of biopolymer in a polyethylene film increases. For example, with a 1.5 % addition, the difference between EMRT and RT varies within the range of 6-12 % in favour of EMRT while a 6 % addition of biopolymer increases the difference in mechanical strength properties to the range of 30-96 % in favour of EMRT.

When modified rice starch was added in a polyethylene film (1.5 - 6.0 %), its mechanical strength properties were impaired only by 20 % while the similar additions of rice starch impaired the values considerably more, i.e. 60 %.

It can be summarized from table 2 that by virtue of the enzymatic modification of biopolymer it is possible to add in a polyethylene film up to 3 times more biopolymer (see table 2 RT 1.5 % and EMRT 4.5 %) to obtain the same mechanical strength properties for the film as those obtained by the addition of untreated biopolymer.

In table 2 with all dry matter contents of biopolymer, the EMRT film is 5-10 µm thinner than a corresponding RT film.

TABLE 2

The effect of the amount of biopolymer on the mechanical strength properties of a polyethylene film

	RT 1.5 % (dry matter)	EMRT 1.5 % (dry matter)	RT 4.5 % (dry matter)	EMRT 4.5 % (dry matter)	RT 6.0 % (dry matter)	EMRT 6.0 % (dry matter)
Tensile strength KS/PS (MPa)	16.5/14.7	17.4/16.2	13.7/11.6	16.3/16.5	12.1/8.4	15.0/16.5
Elongation KS/PS MPa)	300/550	330/610	240/520	350/610	200/370	260/500
Drop test (g)	125	140	95	130	70	110
Film thickness (um)	80	70	85	75	85	80

Mould-formation tests

Tests were effected according to ASTM standard, STM G 21-70 1980. The test was effected with 100 x 80 mm sized test specimens which were incubated in glass Petri dishes (150 x 150 x 25 mm) for 4 weeks at 28°C. Sufficient relative air humidity in the incubation space was secured by placing a vessel containing saturated KNO_3-solution (Rh 92 %) on the incubator floor. The controls used were test specimens that were not sterilized and not treated with mould suspension. The organic nature of mould suspension was checked with standardized test dishes. The mould-formation of plastics was observed at one-week intervals. The test fungi were as follows

Aspergillus niger	ATCC 9142
Penicillium funiculosum	ATCC 11797
Chaetomium globosum	Chg K25
Aureobasidium pullulans	PULL U2

The mould-formation of test specimens was rated visually and microscopically as follows:

0	no growth
1	less than 10 % of surface area
2	10 - 30 % of surface area
3	30 - 60 % of surface area
4	60 - 100 % of surface area

The enclosed table 3 shows that the mould-formation in a compsition having enzymatically modified rice starch was more vigorous than with a polyethylene film having unmodified rice starch added therein.

TABLE 3

The average mould-formation of test specimens

Test specimen	1 week x	2 weeks x	3 weeks x	4 weeks x
LD-polyethylene	0,3	1	1	1
LD-polyethylene + RT 14 %	0,7	1,7	2	2
LD-polyethylene + EMRT 14 %	1	1,3	2	2,7
LD-polyethylene + EMRT 10 % + UV 3 %	1,3	2,3	2,7	3,3

RT = rice starch
EMRT = enzymatically modified rice starch
UV = photosensitive component (Sarmalyte 24000)

It should be appreciated that a biologically decomposable composition of the invention can also be processed into a product by the application of other processes prior known in plastics manufacturing, such as injection moulding, blowing technique, extrusion moulding, vacuum moulding, rotational casting or various foaming techniques. The examples deal with blown films for the reason that the manufacturing of a thin-walled film is in technical sense most demanding, particularly in view of the workability of a biologically decomposablw composition. Generally speaking, such plastics manufacturing t chniques can be appli d which facilitate the manufacturing of an end product at such t mperatures

that an enzymatically modified biopolymer maintains its characteristics promoting the decomposition of a composition in certain conditions. The upper limit temperature range can be considered to be 220-250°C.

In the examples, the synthetic polymer comprises polyethylene. It should be obvious to a person skilled in the art that polyoleophines overall are included in those synthetic polymers that can be employed in a composition of the invention. The agents belonging in the group of polyoleophines include e.g. HD-polyethylene, LD-polyethylene and polypropylene. It is obvious to a skilled person that e.g. polystyrene is a synthetic polymer suitable for a biologically decomposable composition of the invention.

Furthermore, the examples deal with rice starch for the reason that, in unmodified condition, they have the smallest particle size of all known starches. Thus, rice starch provides for the best comparative results in unmodified form. It is self-evident that also corn starch etc. can be used as a biopolymer of the invention. Enzymatic modification makes it possible to reduce their particle size as desired. As far as starch is concerned, it can be said that enzymatic modification provides for such a particle size distribution in which the mean particle size is smaller than 10 µm. As for cellulose, it can be said that enzymatic modification provides for such a particle size distribution in which the mean particle size is smaller than 20 µm (fig. 1).

Claims

1. A biologically decomposable composition, comprising a composition consisting of a biopolymer and a synthetic polymer, the composition further including a material causing in certain conditions disintegration of the chains of the synthetic polymer and/or the synthetic polymer of the composition having been treated in a manner that the chains of the synthetic polymer disintegrate in certain conditions, c h a r a c t e r i z e d in that the biopolymer is enzymatically modified.

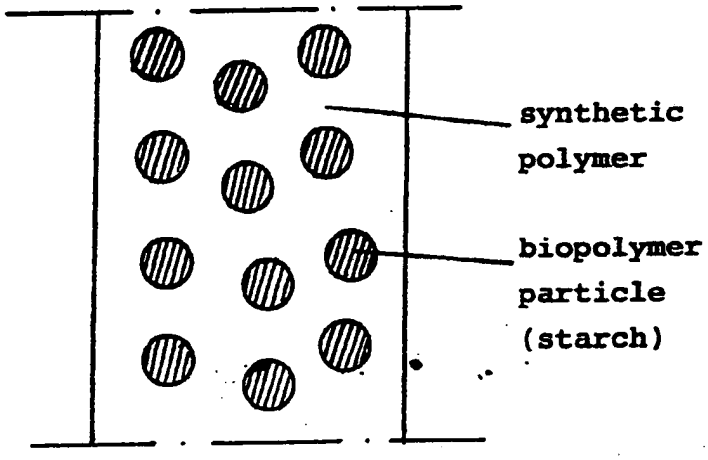
2. A biologically decomposable composition as set forth in claim 1, the biopolymer comprising starch, c h a r a c t e r i z e d in that the enzymatic modification of starch is effected with alfa-amylase, especially with heat-resistant alfa-amylase.

3. A biologically decomposable composition as set forth in claim 1, the biopolymer comprising cellulose, c h a r a c t e r i z e d in that the enzymatic modification of cellulose is effected with cellulase, especially with cellodextrines-forming cellulase.

4. A biologically decomposable composition as set forth in claim 2, c h a r a c t e r i z e d in that the mean particle size of enzymatically modified starch is smaller than 10 um.

5. A biologically decomposable composition as set forth in claim 3, c h a r a c t e r i z e d in that the mean particle size of enzymatically modified cellulose is smaller than 20 um.

a


synthetic
polymer
biopolymer
particle
(starch)

b

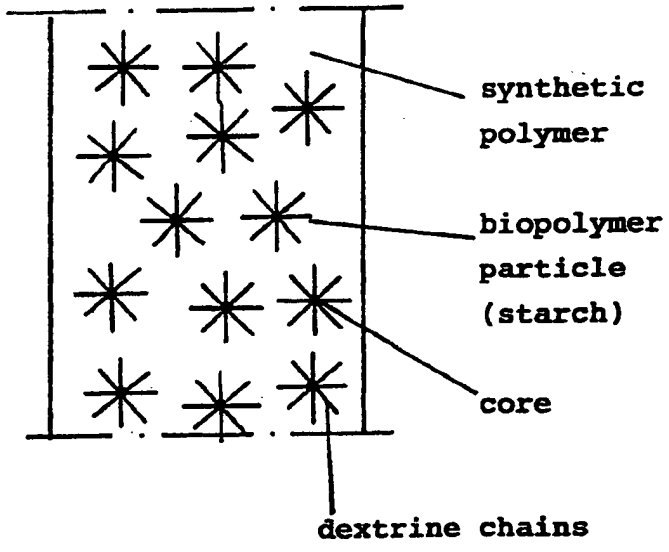
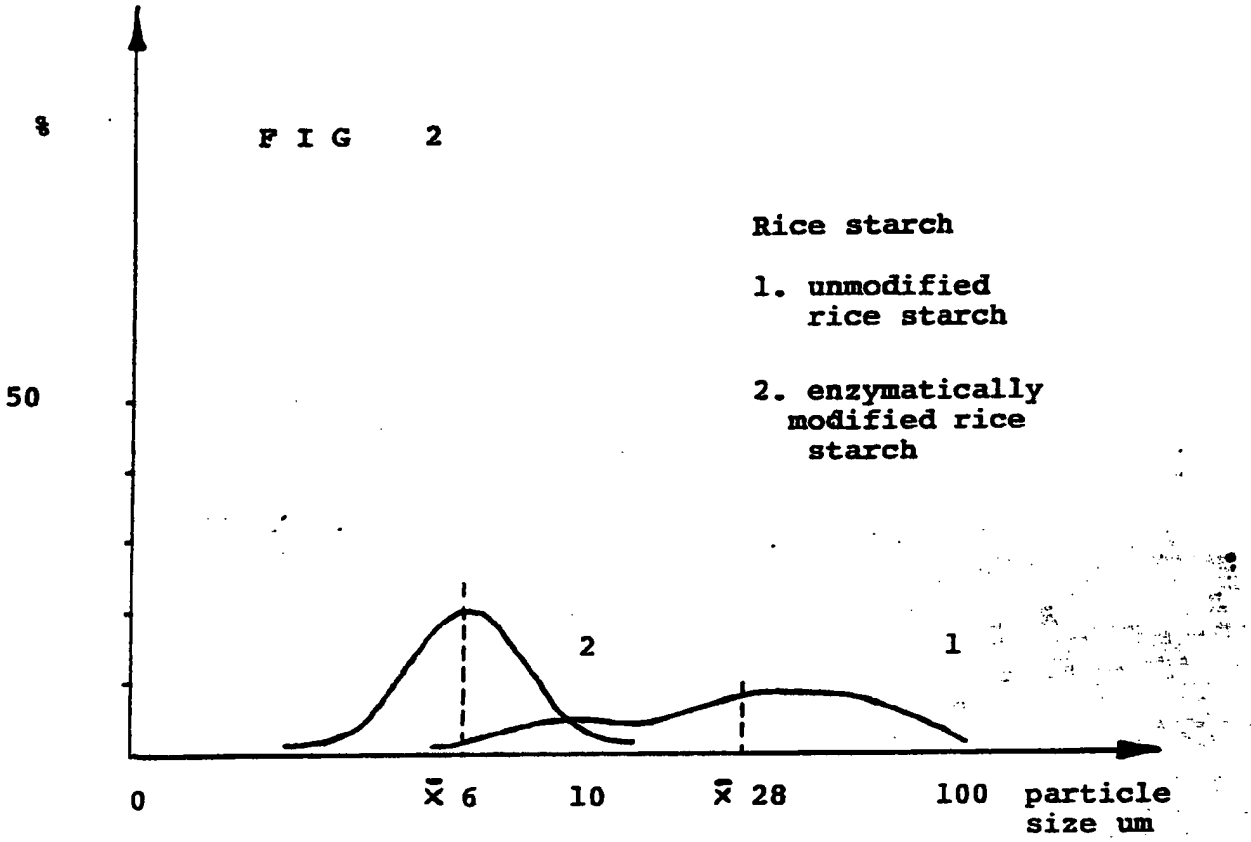
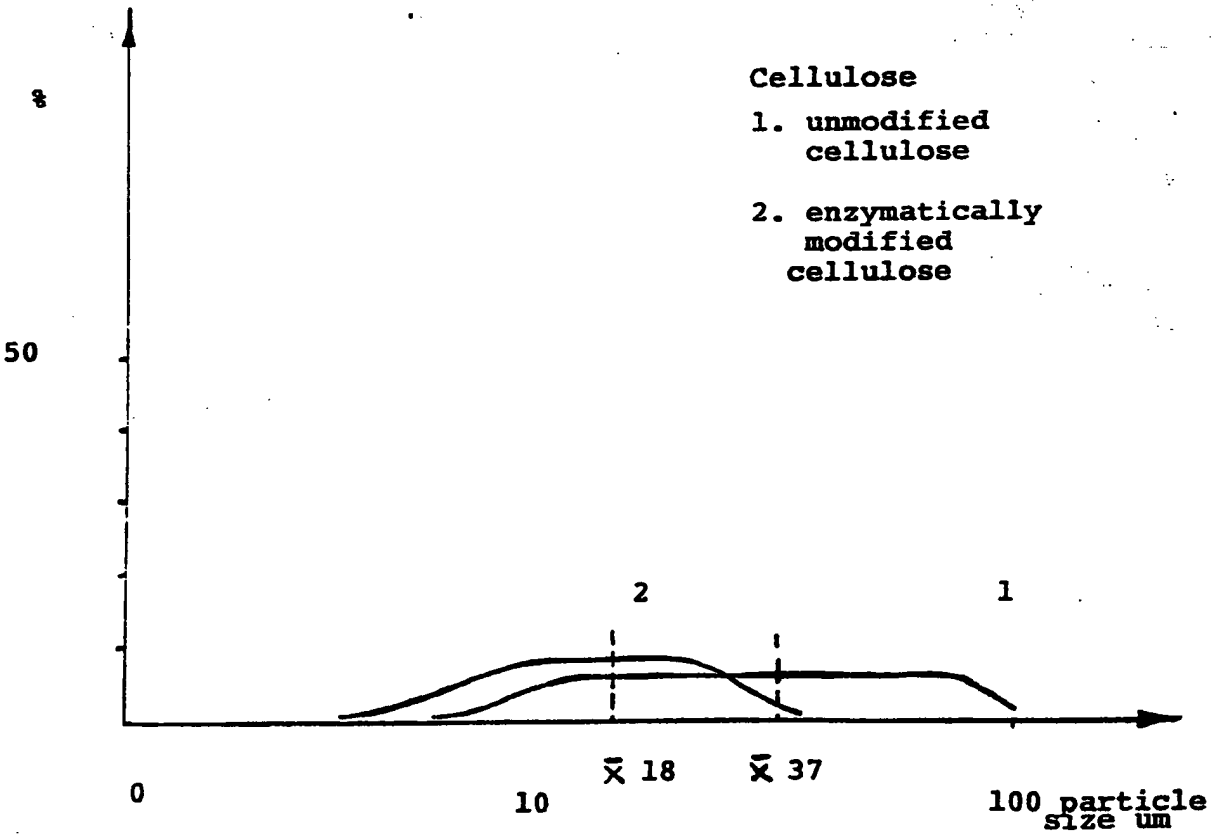

synthetic
polymer
biopolymer
particle
(starch)
core
dextrine chains

FIG 1

FIG 2


%
50
Rice starch
1. unmodified rice starch
2. enzymatically modified rice starch
2
1
0
x̄ 6
10
x̄ 28
100
particle size um


%
50
Cellulose
1. unmodified cellulose
2. enzymatically modified cellulose
2
1
0
10
x̄ 18
x̄ 37
100
particle size um

INTERNATIONAL SEARCH REPORT

International Application No PCT/FI89/00075

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC 4

C 08 L 3/02, 23/06

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC 4	C 08 L 1/00 - 1/02; 3/00 - 3/04; 23/06
US Cl.	260: 896-897; 523: 128; 525:240

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

SE, NO, DK, FI classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [10]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
Y	SE, B, 454 444 (ROQUETTE FRERES SA) 2 May 1988 page 4, lines 19-33 and claim 1 & BE, 893616 FR, 2508051 SE, 8203876 DE, 3223443 JP, 58005376 GB, 2112408 US, 4632848 CA, 1217394 AU, 565280	1-5
Y	EP, A, 0 032 802 (THE SECRETARY, U.S. DEPARTMENT 29 July 1981 page 4, lines 33 - page 5, line 3 and the claims & JP, 56149444 US, 4337181 CA, 1171579	1-5

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"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
1989-07-26	
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Swedish Patent Office	Dagmar Järvman

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